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PATENT SPECIFICATION

DRAWINGS ATTACHED

1,174,959

1,174,959

Date of Application and filing Complete Specification: 14 Sept. 1967.

No. 41987/67.

Application made in United States of America (No. 580048) on 16 Sept., 1966.

Complete Specification Published: 17 Dec., 1969.

Index at acceptance: —**B5** B(2AY, 2CY, 2M12, 2MY, 2P1, 2P4, 2PX, 12, 20BX); **C1** A(E5K1, K4); **C1** M(3A, 3D5, 3D6, 7F19, 7F20, S9A, S9B); **C3** P(8A, 8C8C, 8C14B, 8C17, 8D3A); **C3** R(1C1, 1C5B1, 1C6AX, 1C6X, 1C22, 1L6D, 22C1, 22C5B1, 22C6AX, 22C6X, 22C22, 22L6D); **D1** W(4, 7B)

International Classification: —**D 01 f 7/02, 7/04**

COMPLETE SPECIFICATION

Whisker Orientation and Shaped Bodies containing Uniaxially Oriented Whiskers

We, THE CARBORUNDUM COMPANY, of Niagara Falls, New York, United States of America, a Corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to orientation of whiskers, and more particularly to processes for producing bodies or shaped structures which comprise whiskers in substantial uniaxial orientation and to the bodies formed by said processes.

"Whisker" is a term which is commonly used to refer to a discontinuous, acicular, single crystal fiber. Whiskers generally have a diameter of the order of magnitude of 1μ, although whiskers with diameters as great as ... or more and as small as 100Å or less

It is reported that whiskers of 30 elements and more than 50 compounds have been grown [Nadgornyi, The Properties of Whiskers, Soviet Physics Uspekhi, 5 (3), 462 (1962)], and much effort is being directed to the production of whiskers of additional substances. Among the elements which have been produced in whisker form may be mentioned B, C, Si, Al, Be, Te, Zn, Cd, Cu, Fe, Co, Ti, Sn, Mg and Ag. Metal alloys which have been prepared in whisker form include brass and copper-silver alloys. In addition to the foregoing substances, a variety of inorganic compounds have been produced in whisker form including, for example, B_4C, Al_2O_3, ZnS, Si_3N_4, TaC, MoO_3, SiO_2 and SiC. The last-mentioned is one of the better known, being one of the few materials available commercially in whisker form.

Many of the metallic and inorganic non-metallic whiskers of the types mentioned possess extraordinary mechanical properties, particularly extremely high strength which may

PATENTS ACT 1949

SPECIFICATION NO. 1,174,959

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to Specification Nos. 1,096,457 and 1,128,321.

THE PATENT OFFICE
26 November 1971

R 5390/3

The term "whisker" is used in this specification to mean an acicular single crystal characterized by a large aspect ratio and a high degree of crystal perfection.

substantially to the structural strength of the matrix, are of particular interest as structural materials for aero-space applications, since the potential high performance charac-

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Whisker Orientation and Shaped Bodies containing Uniaxially Oriented Whiskers

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The invention relates to orientation of whiskers, and more particularly to processes for producing bodies or shaped structures which comprise whiskers in substantial uniaxial orientation and to the bodies formed by said processes.

"Whisker" is a term which is commonly used to refer to a discontinuous, acicular, single crystal fiber. Whiskers generally have a diameter of the order of magnitude of 1μ, although whiskers with diameters as great as 25μ, or more and as small as 100Å or less have been reported. Whiskers are, in general, characterized by a high degree of crystal perfection and a large aspect (length to diameter) ratio which ordinarily is at least of the order of magnitude of 10 and may be as high as about 10,000 but more often is in the range from about 100 to about 1000. While whiskers as long as 1 cm or more have been reported, they seldom exceed about 5 mm in length and more often are about 1—3 mm long or less. The longer lengths are frequently associated with larger diameters.

The term "whisker" is used in this specification to mean an acicular single crystal characterized by a large aspect ratio and a high degree of crystal perfection.

It is reported that whiskers of 30 elements and more than 50 compounds have been grown [Nadgornyi, The Properties of Whiskers, Soviet Physics Uspekhi, 5 (3), 462 (1962)], and much effort is being directed to the production of whiskers of additional substances. Among the elements which have been produced in whisker form may be mentioned B, C, Si, Al, Be, Te, Zn, Cd, Cu, Fe, Co, Ti, Sn, Mg and Ag. Metal alloys which have been prepared in whisker form include brass and copper-silver alloys. In addition to the foregoing substances, a variety of inorganic compounds have been produced in whisker form including, for example, B_4C, Al_2O_3, ZnS, Si_3N_4, TaC, MoO_2, SiO_2 and SiC. The last-mentioned is one of the better known, being one of the few materials available commercially in whisker form.

Many of the metallic and inorganic nonmetallic whiskers of the types mentioned possess extraordinary mechanical properties, particularly extremely high strength which may be in the neighbourhood of 70,300 kg/sq cm in some cases. This high strength, coupled with the stiffness, low weight and thermal resistance possessed by many whiskers, has generated much interest in the use of whiskers for the formation of whisker containing bodies, i.e. bodies comprising whiskers incorporated in a non-flowable or solid matrix, the matrix being a synthetic resin, or other polymeric substance, metal, ceramic or other like material. Whisker reinforced bodies i.e. whisker containing bodies wherein the whiskers contribute substantially to the structural strength of the matrix, are of particular interest as structural materials for aero-space applications, since the potential high performance charac-

teristics of such bodies may well satisfy the demanding requirements of that field.

It is generally accepted that optimum reinforcement in a whisker reinforced body is not attained by the incorporation of randomly oriented (i.e unoriented or unaligned) whiskers in the matrix, and that one important consideration in achieving optimum reinforcement and making the best use of the mechanical properties of whiskers is that the whiskers be substantially uniaxially oriented or aligned in the matrix; that is to say that most, if not all, of the whiskers should be so disposed in the matrix that their longest axes approach or achieve parallelism. A major obstacle which has delayed the commercial utilization of whiskers for the production of whisker reinforced bodies has been the lack of an effective and convenient method of achieving such orientation and of producing whisker reinforced bodies in which the whiskers are substantially uniaxially oriented. The novel processes and products of the present invention provide a practical and commercially feasible solution to this problem.

According to the present invention there is provided a process for the production of bodies or shaped structures including a non-flowable matrix having substantially uniaxially oriented whiskers dispersed therein, comprising the steps of forming a dispersion of whiskers (as defined herein) in a flowable dispersion medium which comprises a matrix-forming material, causing said dispersion to flow as a liquid stream and constricting said liquid stream so as to orientate the whiskers are substantially uniaxially in the liquid stream, and solidifying said liquid stream.

Preferably, said constriction is formed by extending said dispersion through an orifice.

An example of the present invention will now be described with reference to the accompanying drawing which is a schematic illustration of apparatus for carrying out the process according to the present invention.

Example 1

20 g. of polyacrylonitrile (PAN) (Orlon a Registered trademark of E. I. du Pont de Nemours & Co.) is dissolved in 80 g. of N,N - dimethylformamide to form a solution having a concentration of 20 percent PAN. The viscosity of this solution is 10,400 centipoises (cp) as determined with a Brookfield viscosimeter employing Spindle #3 at a speed of 2.5 rpm; all viscosity values mentioned herein were determined by the same method at 25°C, except as otherwise stated. To the solution is added 5 g. of silicon carbide (SiC) whiskers having an average length of about 100μ and an average diameter of about 1—2μ, and the mixture is stirred thoroughly to break up any agglomerates and disperse the whiskers.

Referring now to the drawing, the whisker dispersion 10 is placed in a vessel 12 which is supported by a clamp 14 attached to a support stand 16. The bottom of the vessel 12 is provided with an axial outlet 17 having a circular orifice 18 that has a diameter of 4.0 mm and is disposed slightly above the surface of a bath 20 consisting of a water-acetone mixture in a 3 : 4 volume ratio contained by a reservoir 22.

The viscous whisker dipersion 10 flows slowly as a liquid stream through the constricting orifice 18 into the bath 20 which coagulates the PAN, at least on the surface of the liquid stream, thereby forming a non-flowable but deformable filament 24. As a result of gravity and the tension exerted on the coagulated PAN filament by means hereafter described, the diameter of the stream of PAN solution is reduced before it enters the bath whereby the filament 24 is materially smaller in diameter than the diameter of the orifice 18. The filament 24 is pulled through the bath around submersion rods 26 and 28 which hold the filament under the surface of the bath, and then is dried as it passes through a dryer 30, of any suitable type. Tension is applied to the filament by a spool 32 on which the filament is wound, the spool being driven by a motor 34 at a predetermined suitable speed, which in this example is a speed sufficient to collect the filament at the rate of about 18 m/min. The resulting product is a dry whisker composite in the form of a filament having a diameter of about 150μ and a total length of about 5500 m, and comprising SiC whiskers incorporated in a PAN matrix.

As may be observed from the enlarged schematic view 36 of a longitudinal section 38 of a short length of the filament 24, the whiskers 40 in the filament are substantially uniaxially oriented with respect to each other and to the longitudinal axis of the filament. This orientation occurs in part as a result of the constriction of the liquid stream as it flows through orifice 18 and in part as a result of the further constriction of the liquid stream as it flows from the orifice to the water-acetone bath. The orientation is preserved in the filament upon coagulation of the PAN.

The proportion of PAN to be incorporated as a matrix-forming material in the flowable dispersion medium will vary to some extent with the precise nature and molecular weight of the particular batch of PAN used. A sufficiently high proportion must be employed to impart sufficient viscosity to the dispersion medium to permit its being formed into a filament, but if too high a proportion is used the viscosity will be too high to permit the formation and drawing of a filament. As regards the particular PAN employed in Example 1, it was found that the preferred range is from about 18 percent to about 22

percent, which amounts impart to the dispersion medium viscosities of about 4000 cp and 20,000 cp, respectively. A portion of 25 percent tended to form a jelly, while proportions substantially below about 18 percent failed to impart sufficient viscosity. On the other hand, somewhat greater proportion may be used to the extent that the molecular weight of the PAN is lower, while conversely, lower proportions may be necessary of higher molecular weight PAN. Accordingly, proportions from about 5 percent to about 30 percent may be used, with due regard to molecular weight.

In general, in the system of Example 1 a viscosity substantially greater than 20,000 cp approaches an excessively high viscosity, while a viscosity of about 2000 cp or less approaches the lower limit, and it is preferable to employ viscosities in the vicinity of the middle of this range, say from about 8000 cp to about 15,000 cp.

The viscosity of the dispersion medium also affects the diameter of the filament, the diameter increasing with increasing viscosity. Since the degree of whisker orientation, i.e. the extent to which the whiskers approach substantial parallelism, tends to increase with decreasing filament diameter, it will generally be preferred to operate in the lower end of the operable viscosity range. Moreover, the rate at which filaments may be formed increases with decreasing viscosity.

In Example, the proportion of whiskers employed was 25 percent to the amount of polymer. In general, it is preferred to incorporate as high a proportion of whiskers as possible, consistent with being able to form a filament and effect the orientation of the whiskers therein, for reasons which will be made apparent hereinafter. In the system of Example 1, a whisker loading substantially in excess of about 30 percent tends to interfere with the forming of an intact filament. Moreover, if the whisker loading is too high, mutual interference of the whiskers as they pass through the orifice tends to inhibit their orientation to some extent. On the other hand, the whisker loading may be increased as the length of the whiskers employed decreases, since the shorter whiskers have less of a tendency to mutually interfere with orientation. As the whisker concentration is increased, however, the drawing rate must, in general, be decreased, since the increased volume of whiskers in the liquid stream will tend to diminish its coherency.

It will be apparent to those skilled in the art that the apparatus illustrated in the drawing is, in essence, the same sort of apparatus that is widely employed to produce filaments of many types of materials such as glass, Orlon (Registered Trade Mark), nylon and rayon, the process generally being referred to as extrusion accompanied by draw-down. Accordingly, many well-known principles will have general applicability to the process of the present invention as exemplified in Example 1. For example, slower drawing rates will usually tend to result in larger diameter filament, as will increased orifice size. With respect to the present invention, however, the orifice size must be sufficiently large to permit the passage of the whiskers, and if it is substantially narrower than the length of the whiskers, the orifice will tend to become plugged with whiskers which are trapped in a horizontal position across the opening. It is apparent that the diameter of the filament must substantially exceed the diameter of the whiskers.

The extrusion process illustrated in Example 1 may be termed a "wet extrusion" process, since a coagulating bath is employed to solidify the constricted liquid stream. Various other methods may be employed to effect the constriction of a liquid stream and form bodies or shaped structures comprising substantially uniaxially oriented whiskers incorporated in a non-flowable matrix in accordance with the concept of the present invention. One such method is a "dry extrusion" process, wherein a liquid stream, for example a suitable solution of a polymer in a volatile solvent, which solution contains whiskers, disposed therein, is extruded through an orifice in substantially the same manner as in Example 1, but wherein no coagulating bath is employed. Instead, the liquid stream is drawn directly from the orifice through an evaporation zone, heated by suitable means, whereby the solvent is removed from the liquid stream by evaporation and a filament comprising substantially uniaxially oriented whiskers dispersed in a non-flowable or solid polymer matrix is obtained. In such a process, it will generally be preferred to carry out the extrusion and drawing in such a manner that the liquid stream is substantially vertical, since the stream is not rendered non-flowable until at least partial passage through the dryer and therefore is susceptible to sagging and breaking if suspended in a horizontal position.

The process in which the solution flows through the orifice under the force of gravity may be modified by effecting this extrusion at higher pressures, particularly if solution of higher viscosity are used. As the liquid stream is constricted upon passing through the orifice, the whiskers tend to become substantially uniaxially oriented. The liquid stream may then be rendered non-flowable by immersion in a suitable coagulating bath or by passage through a dryer, i.e. a wet or dry extrusion process may be employed. In the wet process, the coagulated filament will generally be subjected to a subsequent drying step. Various other means of effecting the necessary constriction of a liquid stream of whisker dispersion and rendering the same

non-flowable will be apparent to those skilled in the art.

It has been found that the degree of whisker orientation which may be achieved by extrusion under higher pressure is, in general, somewhat less than that obtained by extrusion under the force of gravity. After the extrusion process under higher pressure the liquid stream may be subjected to draw down as a result of which, the liquid stream is further constricted before being rendered non-flowable, and the degree of orientation of the whiskers is considerably increased thereby.

In general, the extrusion processes under the force of gravity will result in a sufficient degree of orientation of the whiskers for purposes of whisker reinforced composites, the whiskers being substantially uniaxially oriented. Extrusion processes under higher pressure, on the other hand, may not give the desired degree of orientation, even when draw down is employed in conjunction therewith. However, in the case of polymer filaments wherein the degree of orientation of the whiskers is somewhat less than desired, it has been found that the degree of orientation can be increased in the dry filament by stretching it, in the direction of whisker orientation, at a temperature at or above the glass transition temperature of the matrix-forming polymer. The glass transition temperature is a well-known property of polymers and is discussed in Stille, Introduction to Polymer Chemistry, John Wiley and Sons, 1962. Such stretching results in attenuation of the filament, as well as elongation thereof, and is accompanied by an increase in the degree of orientation of the whiskers therein, usually to a sufficient degree for purposes of whisker reinforced composites.

The following example illustrates an extrusion process coupled with the further steps of drawing the extruded liquid stream and stretching the formed filament.

Example 2

A 420 g. portion of nylon pellets (du Pont "Zytel" (Registered Trade Mark) 101) is dried at about 80°C in a circulating air oven to remove any moisture which may be present, and blended with 71 g. of SiC whiskers such as those employed in Example 1. The blend is placed in an electrically heated screw extruder having a die opening about 3 mm in diameter and the mixture is heated to a temperature of about 260—290°C to form a very viscous melt which is extruded through the die opening. By means of a motor driven spool similar to that shown in the drawing, the extruded liquid stream is subjected to draw-down, as it is extruded, to a diameter of about 0.5—1 mm, being drawn from the extrusion die opening into a water bath which serves to cool the nylon matrix and form a filament which is solid throughout, thereby preserving the whisker orientation which results first from the extrusion and then from the draw down.

Although considerable orientation of the whiskers occurs in this process, the degree of orientation is increased by stretching the filament formed as above at a temperature of about 65—95°C, which exceeds the glass transition temperature of the nylon employed. (It may be noted that some nylon materials have a glass transition temperature below ordinary room temperatures, and with these stretching may be carried out at room temperature). Stretching the filament to 3 or 4 times its original length resulted in a filament having a diameter of about 150—200μ and a degree of whisker orientation comparable to that obtained in the extrusion process of Example 1.

Whichever method is employed to effect constriction of the liquid stream of whisker dispersion, many of the same principles stated above with reference to the wet extrusion process under the force of gravity, are, in general, applicable. In any case, a suitable dispersion medium is required. This must, of course, be flowable under the conditions employed to effect orientation of the whiskers. The medium must also have a viscosity appropriate to the particular orientation method employed and must, of course, not react with the particular whiskers used. It must also be capable of being rendered solid or otherwise non-flowable, once the whiskers have been oriented, so as to preserve, the oriented disposition of the whiskers. Thus, for example, when a polymer such as nylon is employed as a melt, mere cooling will serve to cause solidification. Where a solution of a polymer or resin in a solvent is employed, a non-flowable state may be achieved, for example, by evaporation to remove the solvent or by coagulation of the polymer or resin. Similarly, molten glass may be used as the dispersion medium and conventional glass extrusion techniques may be used to produce filaments comprising substantially uniaxially oriented whiskers incorporated in a glass matrix.

The dispersion medium must comprise a matrix-forming material, i.e. a material capable of forming a non-flowable or solid matrix in which the oriented whiskers are to be incorporated. When a melt such as nylon or glass is employed as the dispersion medium, the molten material itself ordinarily constitutes the matrix-forming material since upon cooling the material solidifies to form a solid matrix having oriented whiskers incorporated therein. Alternatively, the matrix-forming material may be a substance such as a polymer, which is dissolved in a suitable solvent and which after orientation of the whiskers may be rendered solid or non-flowable by evaporation of coagulation. Suitable polymers and resins include polyacrylonitrile, polymethyl-

methacrylate, poly(ethylene maleic anhydride), polyimides, and phenolics. It is highly desirable that the polymer be linear with little or no cross-linking, the cross-linking tending to interfere with the orientation of the whiskers. Suitable solvents may be selected from a wide variety, depending upon the solubility of the particular polymer chosen. Water, dimethylformamide and acetone have been found to be particularly suitable for use with polymers which are soluble therein.

The particular dispersion medium selected will depend upon various factors, including the particular method of whisker orientation to be employed. Polyacrylonitrile dissolved in a suitable solvent such as dimethylformamide is one of the more useful dispersion media for wet extrusion, since polyacrylonitrile is insoluble in many solvent and thus is readily coagulated. Poly(ethylene maleic anhydride) dissolved in a suitable solvent is not only suitable for dry extrusion when used alone, but if an epoxy resin is also incorporated in the dispersion medium, the filament which results from extrusion may be heated to cure the matrix having oriented whiskers incorporated therein. Acetone is especially usefull as a solvent in dry extrusion due to its volatility. It is desirable to avoid the use of water as a solvent for poly(ethylene maleic anhydride) because of the tendency of the anhydride to react with water.

Various modifications of the methods described and contemplated are possible. For example, it is obvious that spinnerets having a number of orifices may be employed in extrusion processes to produce numerous filaments simultaneously.

The physical form of whisker composites containing substantially uniaxially oriented whiskers has been illustrated hereinabove with particular reference to a filamentous form of more or less circular cross section. However, a variety of other thin, attenuated forms such as ribbons, tapes, sheets and fibres are also contemplated and may be formed by various means. For example, the wet extrusion method under the force of gravity lends itself to the formation of whisker composites in the form of ribbons or tapes. One simple means of accomplishing this result is to employ an orifice which is elliptical rather than circular. It will be apparent that this variation is limited in respect of the longer axis of the elliptical orifice, which must be sufficiently short to effect the requisite constriction for orientation of the whiskers. Another method of forming whisker composites as ribbons or tapes by a wet extrusion process under the force of gravity is to minimize the distance between the orifice and the surface of the coagulation bath, whereby the diameter of the filament is maximized due to coagulation of the liquid stream as it emerges from the orifice. The filament, although non-flowable, is deformable and is flattened somewhat to assume a ribbon-like form as it moves across the first submersion rod in the coagulation bath.

Whisker composites in the form of sheets may be formed, for example, by simultaneously orienting the whiskers in a plurality of liquid streams which are aligned side by side in a single plane and passed between opposing compression rollers which flatten the liquid streams and cause them to contact and cohere along their edges.

While the inventive concepts have been illustrated in the examples with particular reference to SiC whiskers, it should be noted that this material was selected as a matter of convenience due to the ready availability thereof, and that any whiskers may be employed. The particular whiskers used will, of course, be selected with regard to their properties in view of the particular end use contemplated for the oriented whiskers. Moreover, the processes of the invention are equally applicable to certain materials which, while not often designated by the term whiskers none the less conform to the whiskers as hereinabove defined; short fiber asbestos is one such material. It is meant, however, to exclude organic materials in whisker or other fibrous form, since such materials are generally not suited to the formation of composites having the desired properties of structural strength and refractoriness.

The process of the present invention is not substantially adversely affected by the presence in the whiskers or other fibers of finely divided, particulate, non-fibrous materials, since such extraneous matter does not materially affect the orientation of the fibers unless the particle size thereof is more than about one order of magnitude greater than the diameter of the fibers. Thus, particulate impurities in whiskers to be oriented, if of small particle size, are not objectionable. Indeed, this fact provides the basis for a further important modification of the invention in that it is possible to form whisker composites containing not only substantially uniaxially oriented whiskers, but one or more additional particulate materials.

For example, finely divided metal powder may be incorporated with the whiskers in the dispersion medium and a whisker composite containing metal powder obtained. Similarly, finely divided particles of glass, ferrites or other ceramics may be incorporated. The full advantage of such procedures will be pointed out hereinafter.

The whisker composites prepared in accordance with the processes of the invention as described above are generally in the form of filaments, tapes, ribbons, sheets or other similar thin, attenuated bodies which comprise substantially uniaxially oriented whiskers incorporated in a non-flowable or solid matrix.

Such bodies may be employed in various ways. For example, they may be used directly to make whisker reinforced composites by assembling a plurality of filaments, sheets or the like and subjecting the aggregate to conventional processes such as compression molding to produce a whisker reinforced composite body of the desired shape in which the whiskers are substantially uniaxially oriented. When the whisker composites are so employed, it is apparent that the matrix-forming material of the whisker composites will also constitute the matrix material of the whisker reinforced composite body.

As noted earlier, it will generally be preferred to incorporate as much whisker material in the matrix as possible. This will be done with a view toward obtaining whisker composites in which the polymer or resin matrix contains a sufficient proportion of whiskers to afford the desired level of reinforcement of composite bodies formed from the whisker composites. In some cases, however, it may be difficult or impossible to prepare whisker composites having the desired whisker loading since, as mentioned earlier, high whisker loadings may interfere with the drawing of an intact filament and may also result in mutual interference which tends to inhibit orientation. This problem may easily be overcome according to a further embodiment of the present invention by removing the original matrix from the whisker composite to form a fibrous body which comprises matrix-free, substantially uniaxially oriented whiskers and thereafter impregnating such body with the resin or polymer from which it is desired to form the reinforced composite.

The matrix may be removed by any convenient procedure, such as burning or dissolving it. For example, a bundle of parallelly disposed filaments or ribbons, each comprising an organic polymer or resin matrix having substantially uniaxially oriented whiskers embedded therein, may be placed in a furnace and heated to a sufficient temperature to oxidize the matrix material. The resulting product is a body having substantially the same shape as the original bundle of filaments or ribbons, but consisting essentially only of the non-oxidizable portion thereof, i.e. the substantially uniaxially oriented whiskers. In such a process the substantially uniaxial orientation of the whiskers is preserved and the resulting fibrous body, while not strong, has sufficient coherence to withstand gentle handling and may loosely be referred to as oriented whisker roving or yarn. In a similar manner, sheet-like bodies consisting essentially of substantially uniaxially oriented whiskers may be formed by burning off the matrix from a whisker composite in the form of a sheet or a stack thereof. Alternatively the original matrix may be removed by dissolving it in any suitable solvent, but care must be taken to avoid disruption of the substantially uniaxial orientation of the whiskers. Burning is generally less likely to disturb the orientation and thus is the method of choice. When burning is employed the matrix material must be oxidizable at a temperature somewhat below that at which the whiskers will be effected.

Having thus obtained a body consisting essentially of matrix-free, substantially uniaxially oriented whiskers, a suitable proportion of resin or polymer or other matrix-forming material for the formation of the desired whisker reinforced composite may be used to impregnate the body, to form a whisker composite which will be referred to more particularly herein as a secondary whisker composite. One effective way of accomplishing this without disturbing the substantially uniaxial orientation of the whiskers is by preparing a solution of the desired matrix-forming material and spraying or otherwise applying the same to the whisker body. The solution should have a low enough viscosity to permit its penetration into the body and the interstices between the whiskers, thus achieving substantially uniform distribution. The solvent may thereupon be evaporated to form the secondary whisker composite comprising the desired matrix-forming material having incorporated therein the desired quantity of substantially uniaxially oriented whiskers. Whisker reinforced composites may be formed therefrom by assembling a number of secondary whisker composites in a suitable mold and pressing and curing according to well-known methods. It will be apparent that the matrix-forming material used to make the secondary whisker composite may be the same as, or different from, the original matrix-forming material, and that it may be selected from a wire variety of resins and polymers including, for example, epoxy and phenolic resins and epoxidized novolaks.

Whisker composites in thin, attenuated form which contain, in addition to substantially uniaxially oriented whiskers, one or more particulate substances such as metal powder, ferrites, glass particles or other ceramic materials may also be subjected to heat or a suitable solvent to remove the matrix material, thus forming matrix-free, substantially uniaxially oriented whisker bodies having the particulate material intimately admixed therein. Where it is desired to remove the matrix material by means of heat, however, due regard must be given to the nature of the particulate substance as well as the whisker material, neither of which must be affected materially by the heat. In the case of metal powder incorporated in the whisker composite, which metal would be oxidized if oxidizing conditions were employed to burn off the matrix material, it is preferred to employ as the matrix-forming material a resin which will

depolymerize upon heating and then evaporate, the heating being carried out in a hydrogen or other reducing atmosphere. Suitable resins for this purpose include polymethylmethacrylate and polystyrene.

Matrix-free, substantially uniaxially oriented whisker bodies incorporating one or more additional particulate materials are particularly useful for the preparation of whisker reinforced composites. For example, when glass particles are incorporated in the matrix-free whisker body in a sufficient proportion, whisker reinforced glass composites wherein the whiskers are substantially uniaxially oriented may easily be formed by means which will be readily apparent to those skilled in the art; e.g., an aggregate of the matrix-free whisker-glass bodies may be subjected to sufficient heat and pressure to form an integral body. Similarly, matrix-free whisker bodies having metal particles incorporated therein in sufficient quantity may be processed to form substantially uniaxially oriented whisker reinforced metal composites by hot pressing, cold pressing and sintering or other suitable means. The same considerations apply to reinforced ferrite or other ceramic compositions. Matrix-free whisker bodies containing additional particulate substances may also, of course, be used to prepare whisker reinforced composites with any desired matrix-forming material by the same methods that are employed with matrix-free whisker bodies which do not contain additional particulate material.

Another feature of the present invention is that, having formed a whisker composite comprising an organic polymer matrix such as PAN or rayon having substantially uniaxially oriented whiskers embedded therein, the whisker composite may be subjected to sufficient heat, under non-oxidizing conditions, to pyrolyze the matrix material without removing at entirely, whereby there is formed a whisker composite which comprises substantially uniaxially oriented whiskers incorporated in a carbon matrix. Whisker reinforced carbon composites may be prepared from such bodies by employing conventional methods to compact a plurality thereof into any desired shape. Alternatively, such bodies may be impregnated with a sufficient proportion of any desired polymer, by the method described above for preparing secondary whisker composites, and the resulting secondary whisker composites may then be used to form whisker reinforced composite bodies of any desired shape by conventional methods.

All references herein to percentages refer to percent by weight unless otherwise stated.

WHAT WE CLAIM IS:—

1. A process for the production of bodies or shaped structures including a non-flowable matrix having substantially uniaxially oriented whiskers disposed therein, comprising the steps of forming a dispersion of whiskers as defined herein in a flowable dispersion medium which comprises a matrix-forming material, causing said dispersion to flow as a liquid stream and constricting said liquid stream so as to orientate the whiskers substantially uniaxially in the liquid stream, and solidifying said liquid stream.

2. A process as set forth in claim 1, wherein said constriction is effected by extruding said dispersion through an orifice.

3. A process as set forth in claim 2, wherein said liquid stream, after extrusion, is subjected to draw down and thereby attenuated.

4. A process as set forth in any preceding claim, wherein the liquid stream, consisting of a solution of the matrix forming material in a solvent, is solidified by contact with a liquid which coagulates the matrix-forming material at least on the surface of the liquid stream.

5. A process as set forth in any one of claims 1 to 3, wherein the liquid stream, consisting of a molten matrix-forming material, is solidified by cooling the matrix-forming material.

6. A process as set forth in any one of claims 1 to 3, wherein the liquid stream, consisting of a solution of an organic polymeric matrix-forming material is a volatile organic solvent, is dried by passing the liquid stream thorugh a heated zone to evaporate the solvent whereby the liquid stream is rendered solid.

7. A process as set forth in any preceding claim, wherein said dispersion contains, in addition to whiskers, at least one additional finely divided particulate solid substance.

8. A process as set forth in claim 1, wherein the matrix is an organic polymeric material and the body or shaped structures is heated under non-oxidizing conditions to pyrolize this material without removing it entirely so as to form a matrix of carbon.

9. A process for increasing the degree of uniaxial orientation of the whiskers in body or shaped structure comprising a polymer matrix having uniaxially oriented whiskers embedded therein, the body or shaped structure having been formed as claimed in any one of claims 1 to 8, which comprises stretching said matrix in the direction of whisker orientation at a temperature at least as high as the glass transition temperature of the polymer.

10. A process of making fibrous bodies comprising matrix-free, substantially uniaxially oriented whiskers which comprises removing the matrix-forming material from a body or shaped structure produced as claimed in any one of claims 1 to 9 comprising substantially uniaxially oriented whiskers incorporated in a matrix without materially disturbing the orientation of said whiskers.

11. A process as set forth in claim 10,

wherein the matrix is removed by heating.

12. A process as set forth in claim 10, wherein the matrix is removed by dissolving it in a suitable solvent.

13. A process of making bodies or shaped structures comprising substantially uniaxially oriented whiskers in a form especially adapted to the fabrication of whisker reinforced bodies or shaped structures which comprises impregnating a fibrous body produced as claimed in any one of claims 10 to 12, consisting essentially of matrix-free-substantially uniaxially oriented whiskers with an organic matrix-forming material.

14. A fibrous body consisting essentially of substantially uniaxially oriented whiskers when produced by the method of any one of claims 10 to 12.

15. A fibrous body as defined in claim 14 having an additional particulate substance therein.

16. A fibrous body as set forth in claim 15, wherein the additional particulate substance is metal powder.

17. A fibrous body as set forth in claim 14, in the form of a yarn.

18. A fibrous body as set forth in claim 14 which is sheet-like in form.

19. A body or shaped structure when produced by the method of claim 1 comprising a matrix having substantially uniaxially oriented whiskers embedded therein.

20. A body or shaped structure as defined in claim 19, said matrix having embedded therein an additional particulate substance.

21. A body or shaped structure as set forth in claim 19 in the form of a filament.

22. A body or shaped structure as set forth in claim 19 which is sheet-like in form.

23. A body or shaped structure when produced by the method as claimed in claim 8.

24. A process for the production of bodies or shaped structures substantially as hereinbefore described with reference to the accompanying drawing.

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